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Quantum Dynamical Investigation of Photochemical Reactions Beyond the Born Oppenheimer Approximation

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We focus on the quantum mechanical and quantum dynamical description of photochemical reactions, where we are interested in ultrafast chemical reactions mediated by conical intersections (CoIns) as well as on the manipulation of chemical processes by means of optimally designed ultrashort laser pulses.

As model system for electrocyclic reactions that occur on the femtosecond timescale, we study the lightinduced ringopening of cyclohexadiene (CHD). To do so, we reduce the highdimensional (36) system to sufficiently few reactive coordinates that are relevant for the description of its ultrafast dynamics. With the help of those we derive ab initio potential energy surfaces, which are then used in our quantum dynamical simulations.

In the CHD/hexatriene system at least two CoIns S_1/S_0 are energetically reachable and can be accessed with different branching ratios by varying the initial wavepacket. Results of this "passive" control are presented and we hope to extend our investigations on this molecule to "active" control schemes such as optimal control theory (OCT).

To relate our results and interpretations to a description within a normal mode picture, we derive a formalism that enables us to project the molecules motion in the reactive coordinate space onto its normal modes. This not only provides insight in the validity of a normal mode description in the context of CoIns but can also be a starting point to directly compare our results to an experiment.

Of high practical relevance in radical chain reactions is acetylen. Herein experimentalists would like to selectively prepare vibrational states to demonstrate the potency of a new chemistry with laserlight.

To attack the preparation problem we reduce the molecule's Hamiltonian to the experimentally interesting vibrational modes, which in this case are IR-active. Analysis of the electron density's change during these vibrations indicates highest reactivity when exciting the asymmetric CH-stretch mode.

For distinct populations of the IR-active modes we compute the corresponding potential energy surface and eigenfunctions and then use OCT strategies to calculate laser pulses that can be applicable in an experiment for a state selective preparation of acetylen.

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